Table I. Typical Recoveries of Folpet, Captan, and Captafol: Individual Cleanup and Determination of Each Compound

	sample	fortification level, mg/kg	% recovery ± SD
folpet	grapes	0.04	96.7 ± 12.7 (n = 7)
		0.2	88.7 ± 11.2 (n = 8)
captan	apples	0.04	108.2 ± 13.7 (n = 5)
		0.5	81.6 ± 3.2 (n = 5)
captafol	wheat grain	0.04	96.4 ± 15 (n = 8)
		0.2	89.3 ± 7.6 (n = 6)
	wheat straw	0.1	82.8 ± 5.4 (n = 7)
		0.5	81.7 ± 8.5 (n = 14)
	wheat ears	0.1	82.6 ± 7.5 (n = 8)
		0.5	82.2 ± 8.5 (n = 8)

Table II. Recoveries of Folpet, Captan, and Captafol: Simultaneous Determination

sample	fortification level, mg/kg	% recovery		
		folpet	captan	captafol
grapes	0.04	105	113	92
	0.2	105	95	95
apples	0.04	120	90	113
	0.2	100	85	90
wheat grain	0.04	95	75	92
	0.2	95	90	95
wheat straw	0.1	94	97	94
	0.5	84	94	94

We generally noted that storage of the samples for hours in polar solvents (methanol; ethanol; acetonitrile) resulted in lower recovery values. We therefore took acetone as the extraction solvent, processed the samples rapidly, and only interrupted analysis when samples were dried or dissolved in apolar solvents.

The detector is very sensitive to even minor changes in the mobile phase composition. The samples were therefore evaporated to dryness after the column cleanup and dissolved in the conditioned mobile phase for the final high-pressure LC determination.

No variation in the sensitivity of the detector could be observed for months, once the mobile phase was conditioned through the ion-exchange cartridge of the detector. Absorption and/or decomposition of the compounds on the column have never been observed. As the decomposition of these compounds under gas chromatographic conditions may not be excluded, the high-pressure LC determination combined with the specific and sensitive photoconductivity detection is the analytical procedure to be preferred.

The new method outlined is suitable for the residue determination of folpet, captan, and captafol with limits of determination of 0.02 mg/kg in fruit and of 0.05 mg/kg in other plant materials.

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Gas–Liquid Chromatographic Determination of Residues of Methiocarb and Its Toxic Metabolites with the Flame Photometric Detector after Derivatization with Methanesulfonyl Chloride

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Residues of methiocarb, methiocarb sulfoxide, and methiocarb sulfone were determined by oxidation of the compounds to methiocarb sulfone, hydrolysis of the sulfone to its phenolic form, and then derivatization of the phenol to its mesylate with methanesulfonyl chloride. Residues of the methiocarb sulfone mesylate were then determined with a gas chromatograph equipped with a flame photometric detector operated in the sulfur mode. The procedure was applied to crops of spinach, celery, rhubarb, raspberries, and peas. Average residues in methiocarb-treated crops of spinach and celery were 3.67 and 0.43 ppm, respectively. No detectable residues were found in rhubarb, raspberries, or peas; the lower limit of detection was 0.05 ppm.

Methiocarb [4-(methylthio)-3,5-xylyl methylcarbamate, also known as mesurol] is a carbamate pesticide used on a variety of field, vegetable, and fruit crops. Abdel-Wahab et al. (1966) demonstrated that methiocarb is readily oxidized to its sulfoxide and sulfone metabolites, and these compounds have been shown by Metcalf et al. (1967) to be cholinesterase inhibitors.

Several methods, such as the high-pressure liquid chromatography procedure of Lawrence (1977), the thin-layer–gas chromatographic procedure of Ernst et al. (1975), the microwave emission procedure of Bache and Lisk (1968), and the gas chromatographic procedures of Van Middelem et al. (1965) and Lorah and Hemphill (1974), have demonstrated the detection of methiocarb residues, but none of these methods was applied to the determi-

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nation of the sulfoxide and sulfone metabolites. To date, three GLC procedures based on the use of the flame photometric detector (FPD) have been published that determine methiocarb and its sulfoxide and sulfone metabolites. Of these, the procedures of Bowman and Beroza (1969) and Greenhalgh et al. (1976) are based on the separate determination of methiocarb and its two oxidative metabolites. Separate analysis for several compounds in the same crop not only is more time consuming but also has the possible disadvantage of increased interference from crop extractives or other pesticides. The third procedure (Thornton and Dräger, 1973) is based on the oxidation of methiocarb and methiocarb sulfoxide to the sulfone and determination of the three compounds together as methiocarb sulfone.

Most methylcarbamates have poor GLC characteristics and must be manipulated in some way to improve their analytical qualities, and such is the case with methiocarb and its two oxidative metabolites. In the three previously discussed procedures, the compounds are either hydrolyzed trifluoroacetylated, or silylated prior to GLC analysis.

Maitlen and McDonough (1980) published a procedure for the determination of several carbamate pesticides by mesylation with methanesulfonyl chloride and then determination of the derivative by GLC with the FPD in the sulfur mode. This procedure was demonstrated on methiocarb and its sulfoxide and sulfone metabolites but was not applied to the analysis of residues in crops. The mesylation method not only stabilizes these methiocarb compounds for GLC analysis but also enhances sensitivity by adding an additional sulfur atom to these already sulfur-containing compounds. In the tests reported here, this mesylation procedure, coupled with a modification of the extraction and oxidation method of Thornton and Dräger (1973), was applied to the determination of residues of methiocarb and its sulfoxide and sulfone metabolites in crops of spinach, celery, rhubarb, raspberries, and peas.

In this method, the residues are extracted from crops with a solvent mixture of acetone and dichloromethane. The residues of methiocarb and its sulfoxide and sulfone metabolites are then oxidized with hydrogen peroxide and acetic acid, and the resultant methiocarb sulfone is derivatized to its mesylate form and cleaned up by column chromatography on Florisil. The methiocarb sulfone mesylate is then analyzed by GLC with the FPD in the sulfur mode.

MATERIALS AND METHODS

Chemicals and Equipment. All solvents (dichloromethane, hexane, benzene, methyl alcohol, and acetone) were technical grades redistilled in glass. Other chemicals used were pyridine (Baker's analyzed reagent grade that was refluxed over potassium hydroxide for 1 h and then stored in a dark bottle over potassium hydroxide and magnesium sulfate), methanesulfonyl chloride (Eastman Organic Chemicals), potassium hydroxide (Baker's analyzed reagent grade), anhydrous sodium sulfate (Baker's analyzed reagent grade), glacial acetic acid (Fisher's analyzed reagent grade), hydrogen peroxide, 30% (Malinckrodt analytical reagent grade), sodium bicarbonate (Baker's analyzed reagent grade), cotton (washed with dichloromethane and oven dried at 110 °C), and Florisil PR grade (The Floridin Co., Tallahassee, FL).

Standard solutions of methiocarb and its sulfoxide and sulfone metabolites were prepared by dissolving 0.1000 g of the pure compounds in 500 mL of dichloromethane (1 mL = 200 μg). These stock standard solutions were then diluted as desired.

The gas chromatograph was a Hewlett-Packard Model 5840A equipped with a flame photometric detector fitted with a 394-nm filter for the determination of sulfur compounds. The GLC column was 122 cm × 4.0 mm i.d., glass, packed with Gas-Chrom Q (100–120 mesh) coated with 3% OV-101 and operated at a temperature of 210 °C with a nitrogen flow rate of 60 mL/min.

A water bath maintained at a temperature of 40–45 °C and a gentle stream of dry air (filtered through Drierite) were used for the evaporation steps of this procedure.

Crop Treatment and Sampling. Methiocarb, as a 2% pellet bait, was applied at weekly intervals by hand broadcasting to four plots per crop of spinach, celery, rhubarb, raspberries, and peas at the rate of 1.12 kg of active ingredient per hectare (1 lb/acre) per treatment. Four plots for each crop were left untreated as controls. Crops of rhubard, raspberries, and peas each received five weekly treatments beginning on May 18, June 15, and June 16, 1977, respectively. Crops of celery and spinach received six and eight weekly treatments, respectively, beginning on Aug 30, 1977.

Harvest samples of all crops were taken from each replicated treated and control plot 1 day after the last application of methiocarb. Samples were taken at random from each plot replicate, care being taken to avoid the plot borders. None of the samples were washed, but samples of spinach, rhubarb, and celery were trimmed of roots and/or tops, and then all samples were placed in plastic bags and stored in a freezer until analyzed.

Extraction Procedure. Prior to extraction and while still frozen, samples of spinach, celery, and rhubarb were chopped in a Buffalo chopper. The peas were allowed to thaw enough so that they could be shelled, and then the peas and pods were ground separately in a kitchen-type food grinder. The raspberries were extracted without any prior preparation.

Subsamples of 100 g of each crop were placed in 500-mL conical beakers, and 400 mL of a solvent mixture of 25% acetone and 75% dichloromethane was added. The beakers were covered with aluminum foil and allowed to stand overnight in a refrigerator. The next morning, the sample solutions were allowed to warm to room temperature, stirred 1–2 min, and filtered into a separatory funnel through a funnel plugged with glass wool. A tablespoon of anhydrous sodium sulfate was added to the solutions in the separatory funnel, and the mixture shaken for 1 min and then filtered through a fluted filter paper into a bottle. A 25-g portion of the extract (100 mL) was placed in a 125-mL flask and evaporated to dryness. It was determined that the extracts could be evaporated either in a 40–45 °C water bath with the aid of a gentle stream of dry air or with a rotory evaporator.

Analytical Procedure. The residue in the flask was dissolved in 4 mL of glacial acetic acid and 6 mL of 30% hydrogen peroxide, stoppered, and placed in a 40–45 °C water bath and allowed to stand overnight (16–18 h). The samples were removed from the bath, 20 mL of a solution of 15% methyl alcohol and 85% water was added, and then the solutions was placed in a refrigerator for at least 30 min. The sample solutions were removed from the refrigerator and filtered through a funnel tightly plugged with cotton into a 250-mL separatory funnel, and the sample flask and filtering funnel were rinsed with a total of six 10-mL portions of a 15:85 (%) mixture of methyl alcohol and water. The solutions in the separatory funnels were then extracted 3 times with 50 mL each of dichloromethane, and the alcohol–water solution was discarded. The separatory funnel was rinsed with distilled water, and the 150-mL dichloromethane extract was re-

Table I. Comparison of Residues of Methiocarb, Methiocarb Sulfoxide, and Methiocarb Sulfone in Spinach As Determined with Several Extraction Methods

	extraction methods and residues found, ppm[a]						
replicate no.	Thornton and Dräger method	blending $MeCl_2$	blending acetone–$MeCl_2$[b]	blending CH_3CN–$MeCl_2$[b]	steeping $MeCl_2$	steeping acetone–$MeCl_2$[b]	steeping CH_3CN–$MeCl_2$[b]
1	3.93	1.93	2.27	1.96	1.68	3.60	1.60
2	2.20	2.84	2.35	2.34	2.05	2.22	2.59
3	2.31	2.08	2.99	2.02	2.03	2.97	2.41
4	2.67	2.90	3.31	2.13	2.68	2.32	2.00
5	2.70	2.45	2.50	2.15	2.40	2.70	2.12

[a] The residue values in this table were determined by oxidizing and derivatizing the methiocarb, methiocarb sulfoxide, and methiocarb sulfone and the determining them as one compound, methiocarb sulfone mesylate. [b] All of the mixed solvent systems were prepared on a ratio of 1:3 with the $MeCl_2$ being the larger portion of the mixture.

turned to the separatory funnel and shaken for 2 min with 50 mL of a solution of 6% sodium bicarbonate in water. The dichloromethane solution was filtered through a funnel plugged with cotton and overlaid with sodium sulfate. The filtering funnel was rinsed with two 10-mL portions of dichloromethane and the solutions were evaporated to dryness in the water bath. The resultant methiocarb sulfone was derivatized to the mesylate compound as follows. First, 1 mL of 0.25 N methanolic potassium hydroxide was added, the solution was allowed to stand for 15 min, and then 2 mL of a solution of 5% pyridine in benzene (v/v) was added and the solution was evaporated in a water bath with the aid of a gentle stream of air. Two milliliters of a solution of 1% methanesulfonyl chloride in benzene (v/v) was added, and the flask stoppered and allowed to stand for 30 min. The solution was then evaporated to dryness in a water bath as above. To the residue in the flask, 25 mL of a solvent mixture of 20% acetone and 80% hexane was added and the residue on the bottom of the flask etched with a glass stirring rod.

The sample solution was transfered onto a 15-g column of Florisil (PR grade) with 20 mL of the 20:80 solvent mixture. The column was prewashed with 50 mL of the 20:80 solvent mixture, and the column was plugged on the bottom with a small amount of cotton and on the top with 1.0 cm of sodium sulfate and then cotton. After the sample and transfer solution were absorbed into the top of the column, an additional 25 mL of the 20:80 solvent mixture was added. After this solution had been absorbed into the top of the column, the collection flask was changed and the methiocarb sulfone mesylate eluted from the column with 125 mL of the 20:80 solvent mixture. The solution was then evaporated to dryness in the water bath, and the residue dissolved in the appropriate amount of a solvent mixture of 25% acetone and 75% hexane and stored in a refrigerator until analysis by GLC with the FPD in the sulfur mode.

For determination of the efficiency of the analytical procedure, recovery samples were prepared by the addition of methiocarb, methiocarb sulfoxide, and methiocarb sulfone to separate control samples of the five crops just prior to extraction. For determination of the stability of methiocarb and its metabolites during storage in the freezer, control samples were fortified with these compounds and held in storage until after all the treatment samples were analyzed. These recovery samples were then removed from the freezer and analyzed for determination of deterioration during this storage period.

The extraction procedure of Thornton and Dräger (1973) is somewhat involved, so several shorter extraction procedures were investigated and the results compared with results obtained from the Thornton and Dräger method. Besides the procedure of Thornton and Dräger, the procedures investigated included three blending and three steeping procedures. The procedures were applied to a 100-g homogeneous field sample of spinach replicated 5 times. In the first three procedures, the sample was blended in a Waring Blendor for 4 min with 400 mL solvent solutions of either (1) dichloromethane, (2) a 1:3 mixture of acetone and dichloromethane, or (3) a 1:3 mixture of acetonitrile and dichloromethane. After blending, the solutions were handled in the same manner as previously described in this work. In the steeping methods, the spinach samples were placed in a 500-mL conical beaker along with 400 mL of one of the above solvent systems and allowed to stand overnight in a refrigerator. These solutions were then removed from the refrigerator and handled in the same way as previously described.

RESULTS AND DISCUSSION

Statistical analysis of the results obtained from the various extraction procedures (Table I) showed no significant differences among the extraction methods. During the course of the analysis of the five crops involved in this work, it was found that blending peas with any of the various solvent systems previously discussed produced hard-to-break emulsions. It was also found that recoveries of methiocarb and its metabolites from peas and pea pods were 10–15% lower when solvent systems other than the 1:3 mixture of acetone–dichloromethane was used. The steeping procedure with the acetone–dichloromethane solvent system overcame these problems. This procedure was found not only to be efficient but also was less involved and used less solvents than the procedure of Thornton and Dräger.

In the procedure of Thornton and Dräger, it was stated that the time of oxidation with $KMNO_4$ should not exceed 15 min. This time factor creates a problem when several samples are being analyzed simultaneously. It was also stated that the acetone used in this step could cause a problem of incomplete oxidation if not properly purified. For these reasons, the procedure described by Maitlen et al. (1969) for the oxidation of aldicarb and its sulfoxide and sulfone metabolities was slightly modified and applied to the methiocarb compounds. Not only was the procedure satisfactory but it also enhanced the cleanup of the crop samples being analyzed.

In the field, methiocarb is readily oxidized to its cholinesterase-inhibiting sulfoxide and sulfone, and, in turn, these compounds are hydrolyzed to their relatively inactive phenol analogues. As previously described, the procedure in this paper is based on the hydrolysis of the methiocarb sulfone to is phenol and then mesylation of this phenol. Therefore, it is imperative that the phenol analogues be separated from methiocarb and its sulfoxide and sulfone prior to this derivatization procedure. Standards of the phenol analogues were carried through the analytical

Table II. Recovery of Methiocarb Sulfoxide, and Methiocarb Sulfone from Various Crops Fortified with the Pure Compounds prior to Extraction[a]

crop	ppm added	recovery, % methiocarb	methiocarb sulfoxide	methiocarb sulfone
spinach	3.00	77.0	70.0	97.5
		70.0	73.0	66.5
	1.00	104.0	87.5	94.0
celery	1.00	83.5	85.5	85.0
	0.50	76.7	72.5	70.7
		81.3	98.0	129.3
	0.10	90.0	86.2	98.0
rhubarb	1.00	83.0	92.0	86.0
	0.50	89.3	84.0	92.5
	0.10	93.3	102.3	95.3
	0.05	89.0	91.2	88.1
raspberries	1.00	111.0	113.3	89.3
	0.10	106.5	113.0	116.5
		107.0	102.0	99.5
	0.05	94.0	97.2	93.4
shelled peas	0.50	80.0	102.0	96.5
	0.10	109.3	78.3	77.0
		114.0	79.0	76.0
	0.05	89.5	82.3	80.7
pea pods (green)	0.40	81.1	87.3	93.0
	0.10	109.0	81.0	88.0
		83.0	86.3	89.0
	0.05	88.1	81.1	83.0

[a] The values in this table were determined by oxidizing and derivatizing the methiocarb, methiocarb sulfoxide, and methiocarb sulfone and then determining them as one compound, methiocarb sulfone mesylate.

Table III. Recovery of Methiocarb, Methiocarb Sulfoxide, and Methiocarb Sulfone from Various Crops Fortified with the Pure Compounds and Then Stored in a Freezer for 13 Months prior to Analysis[a]

crop	ppm added	recovery, %[b] methiocarb	methiocarb sulfoxide	methiocarb sulfone
spinach	0.50	60.0	97.5	94.5
		70.0		
rhubarb	0.50	89.0	81.0	110.0
		96.5		
celery	0.50	70.0	92.5	97.5
		94.0		
raspberries	0.50	72.0	92.5	82.3
		73.0		
peas (green, shelled)	0.50	101.0	66.0	72.0
		75.5		

[a] The recoveries were prepared on Dec 4, 1977, and then stored in a freezer until analysis in Jan 1979. [b] The recovery data presented here are based on the fortification of the various crops with methiocarb, methiocarb sulfoxide, and methiocarb sulfone and then analysis of the samples based on the oxidation and mesylation of these compounds and their determination as one compound, methiocarb sulfone mesylate.

procedure and were lost in the oxidation step of the method. This, then is a satisfactory way of separating the relatively nontoxic phenol analogues from the toxic methiocarb compounds.

Results in Tables II and III demonstrate the recovery efficiency of methiocarb and its sulfoxide and sulfone from crops fortified with these compounds just prior to extraction and from crops that were fortified with these compounds and held in frozen storage for 13 months prior to analysis. Data in Table II show that recoveries of methiocarb prepared over a range of 0.05–3.0 ppm averaged 92.2% with a range of 70.0–114.0%. Recoveries of methiocarb sulfoxide averaged 89.3% with a range of 70.0–113.0%, and methiocarb sulfone averaged 91.2% with

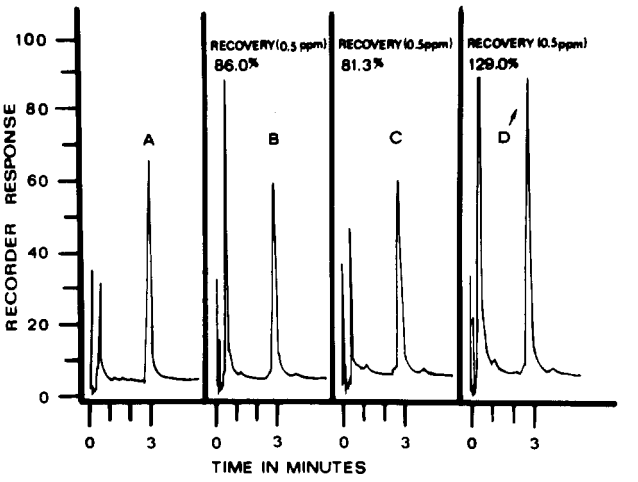

Figure 1. Chromatograms of (A) 10 ng of methiocarb sulfone mesylate and recoveries from celery of (B) methiocarb, (C) methiocarb sulfoxide, and (D) methiocarb sulfone. All recoveries were oxidized and derivatized to methiocarb sulfone mesylate.

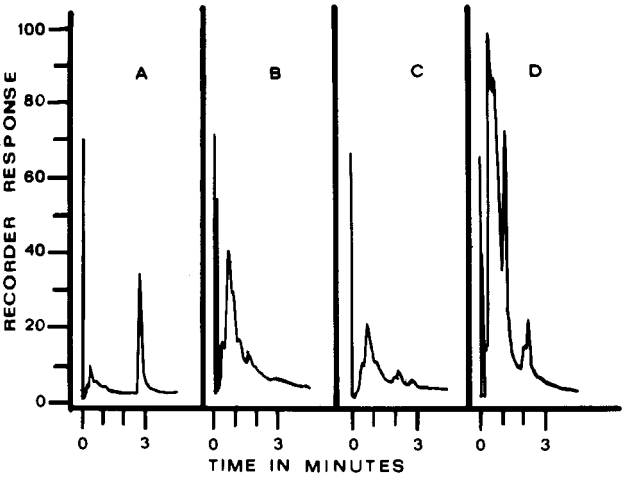

Figure 2. Chromatograms of (A) 5 ng of methiocarb sulfone mesylate and control samples of (B) 0.10 g of raspberries, (C) 0.10 g of rhubarb, and (D) 0.05 g of spinach.

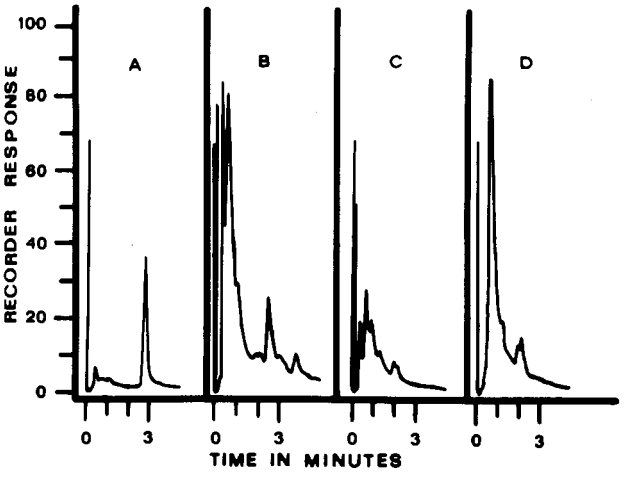

Figure 3. Chromatograms of (A) 5 ng of methiocarb sulfone mesylate and control samples of (B) 0.10 g of celery, (C) 0.10 g of green peas, and (D) 0.10 g of green pea pods.

Table IV. Residues of Methiocarb and Its Sulfone and Sulfoxide Metabolites Found in Various Crops after Weekly Treatments at the Rate of 1 lb of Active Ingredient per Acre[a]

sample	application period (no. of weekly applications)	sampling date	residues found, ppm[b]
spinach			
replicate 1	8/30/70-10/18/77	10/19/77	4.83
replicate 2	(8)		2.93
replicate 3			3.86
replicate 4			3.06
rhubarb			
replicate 1	5/13/77-6/15/77	6/16/77	ND[c]
replicate 2	(5)		ND
replicate 3			ND
replicate 4			0.06
celery			
replicate 1	8/30/77-10/4/77	10/5/77	0.39
replicate 2	(6)		0.55
replicate 3			0.49
replicate 4			0.30
shelled peas			
replicate 1	6/16/77-7/14/77	7/15/77	ND
replicate 2	(5)		ND
replicate 3			ND
replicate 4			ND
pea pods			
replicate 1	6/16/77-7/14/77	7/15/77	ND
replicate 2	(5)		ND
replicate 3			ND
replicate 4			ND
raspberries			
replicate 1	6/16/77-7/14/77	7/15/77	ND
replicate 2	(5)		ND
replicate 3			ND
replicate 4			ND

[a] The residue values in this table were determined by oxidizing and derivatizing the methiocarb, methiocarb sulfoxide, and methiocarb sulfone and then determining them as one compound, methiocarb sulfone mesylate. [b] These values have been corrected to 100% based on recoveries found. [c] ND (none detected) indicates that these residues were below the lower limit of detection for these samples, which was <5.0 ng/aliquot analyzed or <0.05 ppm.

a range of 66.0–129.0%. These recoveries were determined by comparison with their respective oxidized and mesylated methiocarb or sulfoxide or sulfone standard. Comparison of recovery data in Tables II and III shows that differences were not significant between these two sets of data, which indicates that these compounds were stable for at least 13 months when held in frozen storage. Figure 1 is a sample chromatogram demonstrating recoveries of 0.1 ppm of methiocarb, methiocarb sulfoxide, and methiocarb sulfone from celery. The chromatograms are typical of the results obtained in this work and show that the recoveries are satisfactory. Figures 2 and 3 are chromatograms of control samples of raspberries, rhubarb, spinach, celery, geen peas, and green pea pods. These figures show that there are no interfering peaks in the area of the retention time of methiocarb sulfone mesylate.

The results in Table IV show that only spinach and celery contained detectable residues of methiocarb and its toxic methobolites. The combined methiocarb, methiocarb sulfoxide, and methiocarb sulfone residues in spinach samples from four replicated plots averaged 3.67 ppm, and residues in celery averaged 0.43 ppm.

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